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SUMMARY

1. PURPOSE. To provide security and policy review on the document at Tab 1 prior to release to the public.

2. BACKGROUND.

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Tab
1. Copy of manuscript

Recent Advances in Microbial Electrocatalysis

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Abstract

Microbial electrocatalysis is a relatively new field of research in which the intrinsic metabolic capacities of various microbes are coupled with inorganic electrodes to carryout interesting chemical conversions. Given the great diversity in microbial metabolic pathways, a wide variety of processes are possible and have been demonstrated in principle. The generation of electrical currents coupled with the degradation of wastes or the capture of light energy is under extensive investigation. This area has seen the greatest development with an over ten-fold increase in power densities in the past decade. A relatively new development is electrosynthesis, the electrically driven fixation of CO_2 into various chemicals. Moreover, microbial electrochemical devices can be used to carry out desalination or "unbalanced" chemical conversions. Microbial electrocatalysis has the advantages of the exquisite specificity and regioselectivity of biochemical reactions coupled with the robustness and self-duplicating properties of living systems. Here, recent advances in this area are reviewed with significant achievements highlighted. As well, the major factors limiting practical application are discussed along with future directions for improvement.

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Keywords: microbial fuel cell; electrocynthesis; microbial electrocatalysis; desalination; electromethanogenesis

INTRODUCTION

The development of fuel cells, where a fuel is oxidized at the anode, generating a useful electrical current which is used to drive a reduction at the cathode, began with a proposal by Dr. Christian Schöbein in 1838 which was subsequently demonstrated in 1839 by the Welsh scientist Sir William Grove [1]. Additional refinements in the twentieth century, in the 50's and 60's, including the incorporation of a specialized ion exchange membrane composed of sulphonated polystyrene, brought the fuel cell state of the art forward such that it could be used by the NASA space program to supply drinking water and power [2]. Chemical fuel cells are already now in use for portable power, such as remote sensors, cell phones, laptops, and other handheld devices, and are undergoing extensive R&D for the automotive industry, which is evaluating fuel cell technology for use in the hybrid/ zero emissions market.

However, chemical fuel cells often operate at high temperatures using expensive and rare catalysts for oxidation, and require very specific fuels that need to be of high purity to avoid catalyst poisoning. An alternative might be provided by biological catalysts, either microbes (whole cells) or isolated enzymes. In principle, these offer a greater flexibility in that they can be operated at normal temperatures and pressures and use a diverse array of organic fuels. Moreover, microbes contain a variety of enzymes that can naturally catalyze the appropriate fuel redox reactions. In fact, the ability of microbes to produce electrical currents has been recognized for over a century [3, 4], but it is only in the last decade or so that this topic has received wide-spread interest [5-8]. Although microbial fuel cells (MFCs) can be utilized in harvesting electricity from waste and biomass [8] while at the same time carrying out waste treatment [9], they can in fact be very versatile devices capable of being used for desalination [10-13], fixing CO_2 via microbial electrosynthesis and methanogenesis [14-17], and, in principle, allowing electrically driven "unbalanced" microbial conversions [18]. Their range of operational conditions can potentially be extended by incorporating extremophilic organisms allowing for microbial activity under harsh conditions [19].

Thus, recent studies have shown that microbes can plausibly be developed for use as catalysts to generate "green power" in MFCs. In addition, these devices hold the potential promise of sustainability, eliminating the need for toxic or rare catalysts in many applications, using various wastewaters as nutrient source, and producing a wide range of chemical compounds of

commercial interest. In what follows, a short review is presented of some of the potential uses of what can be called Microbial Electrocatalysis Cells (MECs).

MECs-the basics

A microbial electrocatalysis cell is basically a generic electrochemical cell with two electrodes where microbes are used to catalyze reactions at one or more of the electrodes; donating electrons at the anode and accepting electrons at the cathode. These electrode reactions may or may not be separated into different compartments (Fig. 1). A two-cell geometry separates the anodic and cathodic reactions, eliminating some sources of power loss, but introduces internal resistance, adding a potential source of power loss. In any case, either the microbes interact directly with the electrode surface, or are indirectly connected through electrochemical mediators. Direct interaction is to be preferred since it is most likely that this configuration will lead to the highest electron flux. A variety of mechanisms have been described at the molecular level whereby organisms can transfer electrons generated internally through their metabolism to the external electrode [5-8]. These include the biosynthesis of electrically conductive pili, and the synthesis and excretion of mediators that are effective if trapped in the microbial biofilm. Electrogenic organisms (exoelectrogens), i.e. organisms capable of donating electrons at the anode, have been the most studied. Organisms capable of accepting electrons from the cathode exist of course; either normally electrogenic organisms that interact reversibly with electrodes, or organisms accepting electrons from the cathode that are poorly understood at present.

Desalination

Effective desalination processes are of great interest as freshwater supplies are increasingly becoming a limited resource. This ordinarily energy intensive process might well benefit from the application of microbial electrocatalysis technology. Although a number of approaches have been proposed and studied [10, 19-21], most use a variation of a three chamber system which attempts to control pH differences which occur due to microbial metabolic activity. The basic concept is that the potential developed between the anode and cathode is used to either desalinate the water in the middle, third chamber, by drawing anions into the anode and cations into the cathode, or, under the proper conditions, achieving the reverse and desalinating the anode and cathode by drawing cations and anions respectively into the middle chamber. Osmotic microbial

In one study, four MFCs were connected in series hydraulically and their function explored under varying conditions. By operating in a continuous flow mode, wide pH changes were avoided and desalination rates were appreciably increased [10].

Electrosynthesis

MECs can also be used to catalyze CO_2, creating useful chemicals or biofuels which can be of use as renewable energy sources. Greenhouse gases continue to increase to harmful levels due to continued and increasing use of fossil fuels and global land use changes. Photosynthetic organisms in general are natural CO_2 sinks, but ongoing deforestation has greatly decreased terrestrial plant numbers, especially in tropical and rainforest regions. Recent work suggests that microbial electrocatalysis cells could potentially use autotrophic organisms to generate fuels or interesting chemical compounds [14-16, 22-24]. The use of specific organisms, such as the acetogenic *Sporomusa ovata* or hydrogenotrophic methanogens, to electrochemically fix carbon dioxide into acetate or methane has been investigated [14, 16]. Mixed cultures, facultative anaerobic mixotrophic bacteria enriched from different environments, have also been shown to fix CO_2 driven by a cathodic reaction [24-27]. So far the compounds that have been generated, primarily acetate and other organic acids, are of little intrinsic value as commodity chemicals, but these studies have served as a proof of principle. These types of "microbial electrosynthesis" systems, combined with photovoltaics, could extend photosynthetic technology into new areas of synthesis of various organic compounds, replacing the need for costly catalysts and fossil fuel based substrates. Future improvements would be the development of more efficient cathodes, genetic engineering of acetate-producing organisms, and the demonstration of electrosynthesis by a Calvin cycle organism, opening up new biosynthetic possibilities.

Although little studied, another route for CO_2 fixation is the electrically driven microbial reduction to methane, a process that has been called electromethanogenesis [28]. For example, it has been shown that the use of an electrochemical bioreactor can enhance the methane to carbon gas ratio (M/C) of hydrogenotrophic methanogens in anaerobic digester sludge over that seen with a traditional chemical bioreactor [16]. Another variation would be to employ both photosynthetic and electrochemically active organisms in a device to produce clean electrical power, dubbed "Microbial Solar Cells" (MSCs) since they derive their initial power through

solar-driven photosynthetic processes with plants, algae or cyanobacteria fixing CO_2 and delivering organic materials to electrically active bacteria [29].

Wastewater treatment

Wastewater treatment traditionally has used a number of methods to remove pollutants and toxins from effluents. Unfortunately, many of these methods involve physical, biological and chemical processes which can be energy intensive and costly to implement. Many studies have demonstrated that it may be possible to use various configurations of MFC systems and mixed microbial cultures to simultaneously treat wastes and generate sustainable currents [16, 30-34]. Initial studies with these devices have been encouraging in that they have demonstrated current production from wide variety of organic waste streams. Nevertheless, there are serious problems to overcome including; excessive start up times, scale up issues, low power densities and use of expensive, rare catalysts for cathodes.

Photosynthetic Microbial Fuel Cells

Although traditional microbial fuel cells have already shown to have potential future roles in bioremediation and renewable energy production, photosynthetic microbial fuel cells hold great promise for expanding or augmenting their application. Their ability to convert the energy of photons into redox power makes them a good alternative to heterotrophic anodic organisms when organic carbon sources are not readily available. In addition to harnessing this electrogenic potential, oxygenic photosynthesis is also being exploited in biocathodes. Finally, synergistic approaches are being explored to merge the best qualities of traditional MFCs with complementary attributes found in photosynthetic microbes.

Just as the ability of bacteria like *Shewanella* and *Geobacter* to carryout direct electron transport to electrodes is a cornerstone of traditional MFC power, the most straightforward scenario would be to find species of algae, cyanobacteria, or photosynthetic bacteria that could form conductive biofilms directly on anodes. One study in this area examined biofilm formation and mediator-less power production by the freshwater alga *Chlorella vulgaris*, the marine alga *Dunaliella tertiolecta*, the freshwater cyanobacterium *Synechocystis* sp. PCC 6803, and the marine cyanobacterium *Synechococcus* sp. WH 5701 [35]. Under cultivation conditions conducive to biofilm formation, it was found that the majority of cells in each culture were

attached to the ITO-PET electrode with the exception of *Synechocystis* sp. PCC 6803, where even the minor fraction of cells initially attached were easily detached by gentle shaking. Power production was several-fold higher in marine species than in freshwater species, as might be expected due to the superior conductivity of higher ionic strength media. *Synechococcus* also produced approximately twice as much power in the light compared to the dark, whereas the other species displayed only slightly higher power production under illumination. In another study using Synechocystis sp. PCC6803 power generation in a mediator-less MFC was shown, with power production affected by light intensity, light wavelength, and concentration of cyanobacteria inoculum [36]. Power output doubled upon illumination, suggesting the cyanobacteria were indeed transferring electrons generated during photosynthesis.

In another study a three-channel micro-scale fuel cell using minimal reagent volumes was used to analyze the performance of *Synechocystis* sp. PCC 6803 [37]. At equal chlorophyll amounts, whole *Synechocystis* cells had almost double the total power output of isolated spinach thylakoid membranes, mostly due to the fact that power production for *Synechocystis* was higher in the dark than in the light whereas power production with thylakoid membranes was negligible in the dark. This underscores the potential importance of the energy contribution from respiration in photosynthetic organisms. In this study, no energy production was seen without the use of ferricyanide as a chemical mediator; probably necessary as cells were supplied as a suspension rather than as a thick biofilm layer on the anode. Although useful for organelle studies, the small volume of the anode chamber led to complications due to the occasional formation of oxygen bubbles.

In a more recent study, a much larger five-channel BPV system was developed that allowed replicates and an abiotic control to be run simultaneously [38]. Comparison of ITO (indium tin oxide-coated polyethylene terephthalate), SS (stainless steel), PANI (glass coated with a conductive polymer), and CP (carbon paper) anodes revealed markedly higher power outputs in both darkness and light when using ITO, although stainless steel showed the highest percent increase in power output upon illumination. Although current was not measured directly, graphs of polarization data suggest that ITO achieved a much higher current density than the other materials. Surface roughness and surface energy were also measured and it was suggested that the higher energy output with ITO, the smoothest surface, may be due to increased surface

contact with the filamentous cyanobacteria. Of note, carbon paper, although frequently used in photosynthetic MFCs, exhibited the worst performance of the four anodes tested. Carbon has been suggested as a good material for MFC electrodes due to the existence of geobatteries using natural carbon deposits; however, these have been primarily found deep underground and photosynthetic organisms may not have evolved to use them.

A number of studies have been made with the cyanobacterium *Arthrospira platensis*. In one, power density was found to be much lower when illuminated than in the dark, with closer electrode spacing resulting in slightly higher values [39]. OCV (open circuit voltage), maximum current density and maximum power density occurred at a pH of 5.5 compared to 8.3 and 9.9, which they attributed to higher ionic strength of the media. Increasing the temperature from 20 °C to 40 °C also caused large increases in current density and power density. In another study using the same organism, the power outputs generated are amongst the highest reported, but only during a three-hour dark "discharge" phase that was then followed by a 15- hour "regeneration" phase where fresh media and light were used to restore biomass and chlorophyll levels to pre-discharge levels [40]. Relying solely on the dark phase for electricity generation may circumvent problems posed by oxygen evolved from photosynthesis, and the use of six fuel cells in series, with staggered schedules, was suggested in order to provide continuous power generation.

A further study examined the filamentous cyanobacteria *Arthrospira platentis* at differing light intensities and different temperatures (35 °C versus 25 °C) [41]. At 25 °C, both power density and current density increased incrementally when going from dark to light and when doubling the light intensity. At 35 °C, the increase was much greater, with power density during maximum light more than twice as high as during the dark, accompanied by an approximately 50% increase in current density. Power and current density were much higher at 35 °C than at 25 °C. Maximum power output was obtained under the conditions most favorable for growth of *A. maxima*, but, as pointed out, the increased amount of energy production from the fuel cell must be balanced against the increased energy input required to maintain the culture at 35 °C. *A. maxima* might therefore be a good candidate for photosynthetic fuel cells in locations with a high ambient temperature.

Although these initial studies are encouraging, further investigation into the unknown mechanisms of electron transfer in these photosynthetic anodic biofilms will be required in order

to increase significantly current densities. On the other hand, the known capability of algae to carry out photosynthetic oxygen production is being used to develop biocathodes. It has been suggested that traditional MFC studies show that power generation is generally considered oxygen-limited at dissolved oxygen (DO) levels below 6 mg/L [42]. When mechanical aeration was compared to cathodic oxygen production by algae in a device using sludge originally obtained from a wastewater treatment plant at the anode, an average DO of 7.07 $\pm$ 0.25 was found for the air pump whereas a DO of 4.78 $\pm$ 0.72 was found for the algal cathode. The lower voltage and power densities in the algal-cathode MFC were attributed to the lower and more variable DO levels. However, if the decrease in power output by the photosynthetic MFC was smaller in magnitude than the power input required for mechanical aeration, it would still be of net benefit.

A study using *Chlorella vulgaris* and carbon felt or Pt-coated carbon cloth electrodes in the cathode and non-photosynthetic wastewater-isolated cultures for the anode showed that, although DO levels varied considerably with light/dark phase, DO levels as high as 20.81 mg/L were obtained with the Pt-carbon cloth and were much higher in the MFCs with algae than in the abiotic controls [43]. Taken together, these results suggest that algal oxygen production may be a viable alternative to mechanical aeration, especially when the algae used is a strain such as *Chlorella vulgaris* with the potential for extraction of biofuels from the biomass cultivated in the fuel cell. Others examined the use of *Chlorella vulgaris* to generate oxygen in the cathode without using an expensive Pt catalyst. A dramatic improvement in half-cell short circuit current was found when using a composite polypyrrole/ poly(methylene blue) on stainless steel electrode compared to a plain graphite or methylene blue-coated graphite cathode. Power production by a completely biotic yeast-anode/algae-cathode MFC was also demonstrated [44].

Traditional MFCs have long been proposed for uses in wastewater treatment, and it is therefore not surprising that the ability of photosynthetic organisms to contribute to power generation at the anode while remediating wastewater is a popular subject of investigation. When a microaerophilic (DO <0.45 mg/L) fuel cell using a "mixed photosynthetic consortia" was fed with acetate-supplemented synthetic wastewater over six cycles of batch feeding, a general trend of increasing biomass and power output was found with a maximum during the sixth cycle [45]. Power output increased in response to light, and pigment analysis revealed that the population of

photosynthetic organisms shifted from predominantly algae during the first cycle to being increasingly dominated by photosynthetic bacteria during subsequent cycles, not surprising given the supplementation with acetate.

When the performance of a similarly designed fuel cell using a "mixed photosynthetic algal consortia" and an oxygenic environment with domestic sewage allowing mixotrophic growth was compared to the results of the previous study it was concluded that the algal production of oxygen lead to consumption of the electrons produced, resulting in a lower power output [46]. Others have examined the capacity of algae to function in a mixed microbial-algal MFC, generating electricity and removing COD from wastewater, while at the same time taking up nitrogen and phosphorus and accumulating lipids [47]. More than 99% of the acetate was removed with no net CO_2 production, a result attributed to algal CO_2 fixation. Power generation fluctuated on a cyclic basis with alternating light:dark phases and was negligible during operation in constant darkness, indicating that the algal component was integral to the fuel cell's productivity. In a novel use, a MFC was constructed that used water from a lake contaminated by microcystin-releasing blue-green algae as a substrate, simultaneously generating power and greatly reducing nitrogen levels and degrading a high percentage of the toxic microcystins [48].

Although natural consortia, such as those described above, may be productive, it is difficult to decipher the relative contributions of and interactions between the different members of the microbial population. In one study designed to shed light on this, a systematic investigation of a co-culture of *Chlamydomonas reinhardtii* and *Geobacter sulfurreducens* was carried out [49]. Only limited power production was observed in constant light or constant dark conditions. In contrast, steady production was observed during the dark phase of a 12-hr alternating light:dark regime. It seems that power production was primarily due to the donation of electrons to the anode by *G. sulfurreducens* during the anoxic dark phase when it metabolized formate produced during the oxygenic light phase by *C. reinhardtii*. It was suggested that the periodicity of power generation with this defined co-culture as opposed to the continuous power generation with natural consortia indicates that tertiary species may be important in the modulation of interactions between photosynthetic and electrogenic heterotrophic organisms.

Conclusion

Given the vast abundance of solar energy and the superior ability of photosynthetic organisms to capture that energy when compared to manmade solar cells, the use of these organisms in MFCs is undoubtedly an important avenue of research. Progress in this field, however, is hampered by the wildly disparate nature of the experimental conditions and measurements reported in the literature. Power production is reported most commonly in Watts per anode surface area but also in Watts per cathode surface area, per anode compartment volume, or per mole of chlorophyll. Maximum current density and any type of voltage measurement may or may not be reported. In some cases these values had to be estimated from graphs. The use of controls is equally variable, ranging from complete MFCs without the algae to algal MFCs without the electrode/PEM assembly when used at all. The studies covered in this review all have their value, each contributing a kernel of knowledge whether they embody a basic science investigation of different anode properties or seek to validate the application of locally isolated photosynthetic consortia to wastewater treatment. Scientific advancement would be more cumulative and probably progress much faster if a standardized fuel cell setup was agreed upon so different researchers could focus on one or two variables each with the remaining variables at least partially controlled for between laboratories. Given the potential for commercialization and the resultant race to create the most effective MFC, such standardization is unlikely, but an effort to standardize at least the reporting parameters would facilitate the comparison of different studies and promote the collaborative nature of scientific research.

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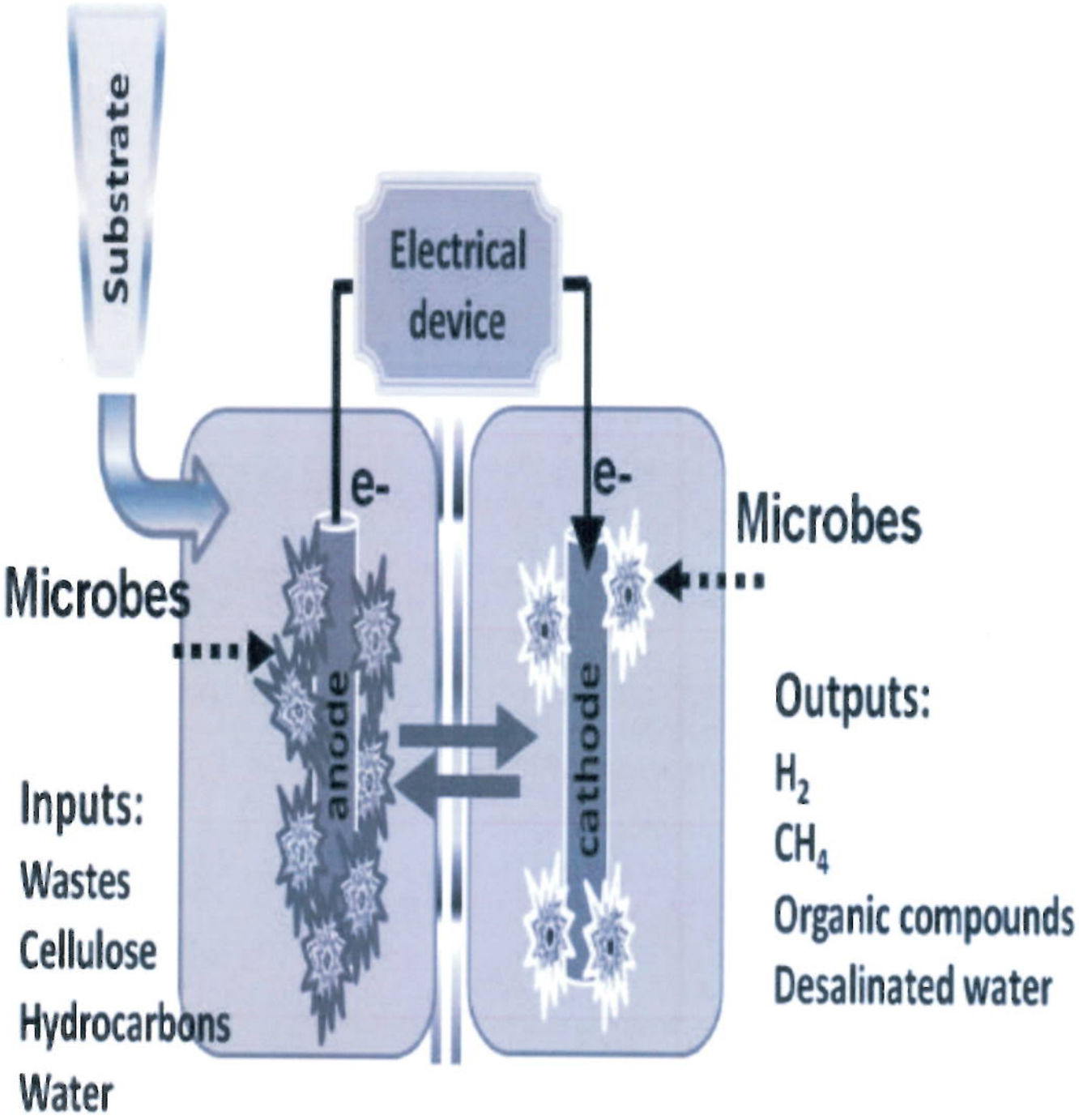
Figure legends

Figure 1. Schematic of MEC (microbial electrocatalysis cell)

A general schematic of a MEC is shown with the two electrodes, anode and cathode, both capable of interacting electrically with microbes depending upon the application. Current passes through a circuit and an electrical device. This can either be something (light bulb, motor) that produces work from the biologically generated current, or it can be a power supply which adds additional current to produce hydrogen, or enable carbon dioxide reduction, at the cathode.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